symmetry

MDPI

Review

Synthesis of Chiral Cyclic Carbonates via Kinetic Resolution of Racemic Epoxides and Carbon Dioxide

Xiao Wu [1,*,†], José A. Castro-Osma [2,†] and Michael North [1]

Received: 18 November 2015; Accepted: 11 January 2016; Published: 14 January 2016
Academic Editor: Svetlana Tsogoeva

[1] Green Chemistry Centre of Excellence, Department of Chemistry, University of York, Heslington YO10 5DD, UK; michael.north@york.ac.uk
[2] Departamento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Instituto Regional de Investigación Científica Aplicada-IRICA, Universidad de Castilla-La Mancha, Ciudad Real 13071, Spain; JoseAntonio.Castro@uclm.es
* Correspondence: xiao.wu@york.ac.uk; Tel.: +44-01904-324547
† These authors contributed equally to this work.

Abstract: The catalytic synthesis of cyclic carbonates using carbon dioxide as a C1-building block is a highly active area of research. Here, we review the catalytic production of enantiomerically enriched cyclic carbonates via kinetic resolution of racemic epoxides catalysed by metal-containing catalyst systems.

Keywords: carbon dioxide; catalysis; metal catalysts; cyclic carbonates; kinetic resolution

1. Introduction

Carbon dioxide is considered to be a cheap, non-toxic and versatile carbon source and its direct chemical fixation has received a great deal of attention in recent years [1–5]. The preparation of cyclic carbonates via the coupling reaction of carbon dioxide and epoxides is one of the most effective routes for carbon dioxide fixation. Although a number of catalyst systems have been developed for this process, only a handful have been used for the enantioselective synthesis of cyclic carbonates. Both enantiopure epoxides and cyclic carbonates are important intermediates because of their versatile reactivity. In particular, stereoselective ring-opening reactions of epoxides with nucleophiles can provide a range of bifunctional compounds, and chiral cyclic carbonates are also valuable building blocks for masked 1,2-diols, polymeric materials and in pharmaceutical and fine chemical synthesis [6–8]. This review will focus on the enantioselective synthesis of a variety of cyclic carbonates from epoxides and carbon dioxide via kinetic resolution.

2. Enantioselective Synthesis of Cyclic Carbonates via Kinetic Resolution of Epoxides

One way to synthesise enantiomerically-enriched cyclic carbonates is via kinetic resolution. In this system, it was proposed that a chiral Lewis acid selectively complexes to one enantiomer of a racemic epoxide. Subsequent attack of a nucleophile or activated carbon dioxide towards the coordinated epoxide then leads to enantioselective ring-opening of the epoxide, with intramolecular elimination providing the enantiomerically-enriched cyclic carbonate. Consequently, the enantiomeric excess of the remaining epoxide would be increased (Figure 1) [9].

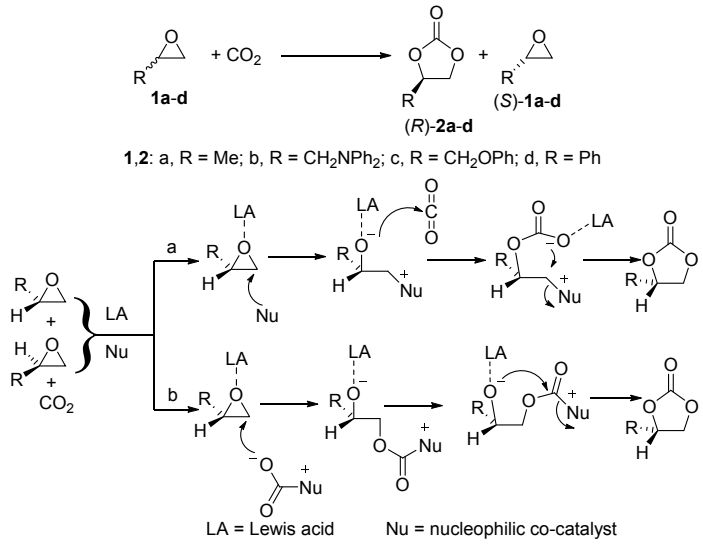

Figure 1. Possible mechanisms for the coupling reaction of carbon dioxide and epoxides.

2.1. Cobalt(III) Salen Complexes

The first example of the preparation of enantiomerically-pure cyclic carbonates via kinetic resolution of epoxides using a cobalt(III) salen complex was reported by Nguyen in 2004 [10]. Propylene carbonate **2a** was produced in up to 68% *ee*, corresponding to a selectivity factor *s* of 5.6, when chiral cobalt(III) complex **3** (Figure 2) and DMAP* [(*R*)-(+)-4-dimethyl-aminopyridinyl (pentaphenylcyclopentadienyl)iron] were employed. Notably, the chiral Lewis base did not contribute significantly to the enantioselectivity. Later, Lu reported the use of a similar cobalt(III)salen complex **4** in the presence of two equivalents of *n*-NBu_4Cl (*n*-tetrabutylammonium chloride) for the synthesis of enantioenriched propylene carbonate **2a** [11]. The bulky *p*-toluene-sulfonate counterion was essential to obtain high enantioselectivity. By replacing the counterion with trifluoroacetyl to give the resulting cobalt(III) complex **5** and employing PPNF [(bis-(triphenylphosphoranylidene)ammonium fluoride)] as co-catalyst, propylene carbonate **2a** was obtained in 40% yield and 83% *ee* at atmospheric carbon dioxide pressure and −40 °C [12]. This corresponded to a significant increase in selectivity (*s* = 18.7).

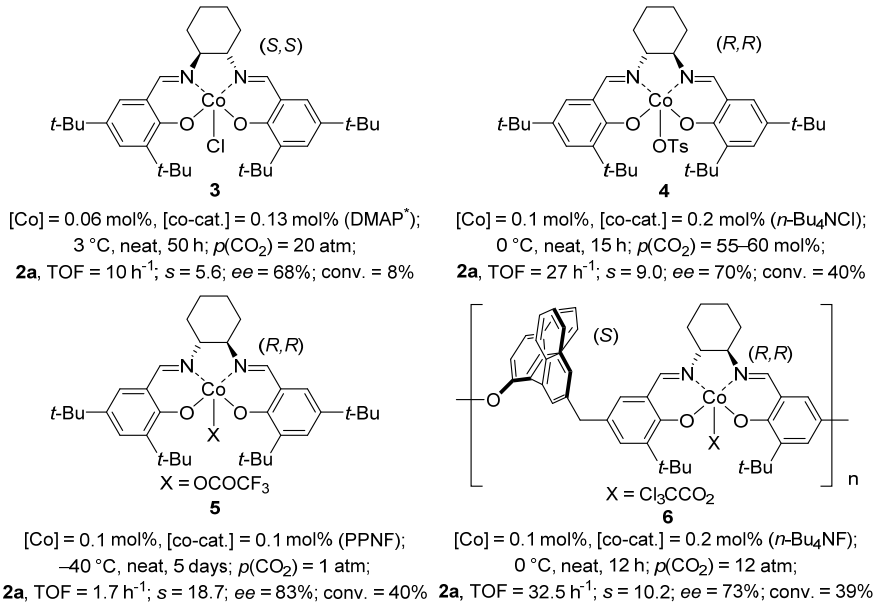

Figure 2. Cobalt(III) salen based catalyst systems for the synthesis of optically active cyclic carbonates.

Since the initial report, a number of modifications to the cobalt(III) salen catalyst system have been reported, all of which demonstrated some degrees of success [13–22]. Jing and co-workers reported a chiral polymer based on BINOL cobalt(III) salen complex **6** for the asymmetric addition of carbon dioxide to racemic propylene oxide **2a** [23]. A comparable enantioselectivity and selectivity factor to that of similar homogeneous cobalt(III) salen systems were reported. Notably, the catalyst could be easily recovered and reused more than ten times without loss of activity or enantioselectivity.

In 2012, Lu and co-workers [24] reported the most effective catalytic system to date for the kinetic resolution of racemic epoxides into enantioenriched cyclic carbonates. This system consisted of a chiral cobalt(III) salen complex **7** (Figure 3) with an (*R*,*R*,*R*)-configured side group as the catalyst and PPN-DNP [(bis-(triphenylphosphoranylidene)ammonium 2,4-dinitrophenoxide)] as the co-catalyst [24]. Propylene carbonate **2a** was obtained in 97% *ee* and *s* value of 76. The variation of the co-catalyst and its relative loading dramatically changed both the selectivity and enantioselectivity of the reaction. Furthermore, the anion and cation of the ammonium-based co-catalysts also significantly affected the enantioselectivity. The use of both a nucleophilic anion with poor leaving group ability and a bulky cation were beneficial for improving the enantioselectivity. The excess co-catalyst loading also favours selective production of cyclic carbonates via the intramolecular elimination of the resultant linear carbonate over the formation of the corresponding polymer. The utility of the catalyst system containing cobalt(III) complex **7** was demonstrated for the conversion of other epoxides such as butylene oxide into its corresponding chiral cyclic carbonate with a *s* value of 31.5 and 88.5% *ee*.

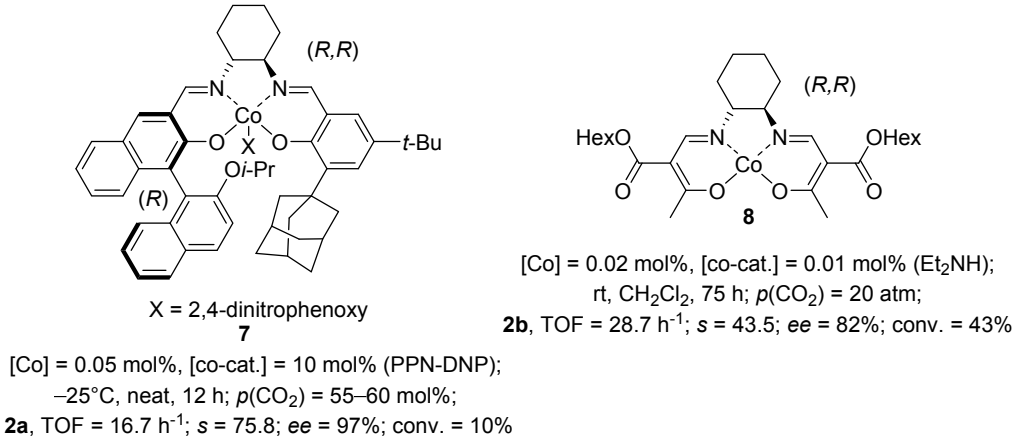

Figure 3. Cobalt(III) and cobalt(II) salen based catalyst systems for the synthesis of optically active cyclic carbonates.

2.2. Cobalt(II) Salen Complexes

Yamada and co-workers reported that the chiral ketoiminatocobalt(II) complex **8** catalysed the enantioselective synthesis of cyclic carbonates [25,26]. Although the combination of complex **8** and diethylamine could work with a range of epoxides, it was found that the catalytic system is substrate dependent, giving the highest *s* value of 43.5 with *N*-(2,3-epoxypropyl)diphenylamine **1b** as the epoxide.

2.3. Other Metal Salen Complexes

Although a number of metal-based salen complexes have been developed [11,18] only a few catalytic systems gave comparable results to that of cobalt-based complexes. Recently, North *et al.* have reported the use of aluminium(III) and chromium(III) salen complexes for the kinetic resolution of terminal epoxides via carbon dioxide coupling (Figure 4) [27]. It is worth highlighting that they have reported the first aluminium-based catalysts capable of performing the kinetic resolution of epoxides by carbon dioxide coupling for the synthesis of enantiomerically enriched cyclic carbonates.

Moreover, aluminium is one of the six most abundant and sustainable metals [28] and therefore makes these catalysts very attractive in a future green chemicals industry. The authors reported that a combination of aluminium(III)(salen) acetate and *n*-Bu_4NBr (*n*-tetrabutylammonium bromide) was the most active and selective catalytic system for the synthesis of optically active cyclic carbonates from racemic epoxides. It was observed that kinetic resolution of epoxides via carbon dioxide coupling was substrate dependent. Hence, when phenyl glycidyl ether **1c** was used as a substrate, 36% conversion and 54% *ee* were obtained at one atmosphere carbon dioxide pressure and 0 °C. However, 15% conversion and 86% *ee* were obtained under the same reaction conditions when *N*-(2,3-epoxypropyl)diphenylamine **1b** was used. These results suggested that the reaction mechanisms occur via a different stereodetermining step. Chromium(III) salen complexes were also investigated for the kinetic resolution of phenyl glycidyl ether **1c**. Firstly, the counterion of the catalyst was investigated using *n*-Bu_4NBr or DMAP as a co-catalyst. This showed that chloride or tosylate counterions on the chromium centre gave enantioselective catalysts though with low *s* values (1.1–2.2). Subsequently, the effect of the co-catalyst was studied and the results showed that a combination of chromium(III)(salen) acetate and PPNCl [(bis-(triphenylphosphoranylidene)ammonium chloride)] was the most efficient catalyst for the kinetic resolution of phenyl glycidyl ether **1c**, achieving 84% conversion and a *s* value of 3.1 at 25 °C and one atmosphere of carbon dioxide pressure for 24 h. Similarly, the use of *N*-(2,3-epoxypropyl)diphenylamine **1b** gave a *s* value of 7.3 when the reaction was carried out at 25 °C and one atmosphere of carbon dioxide pressure for 3 h.

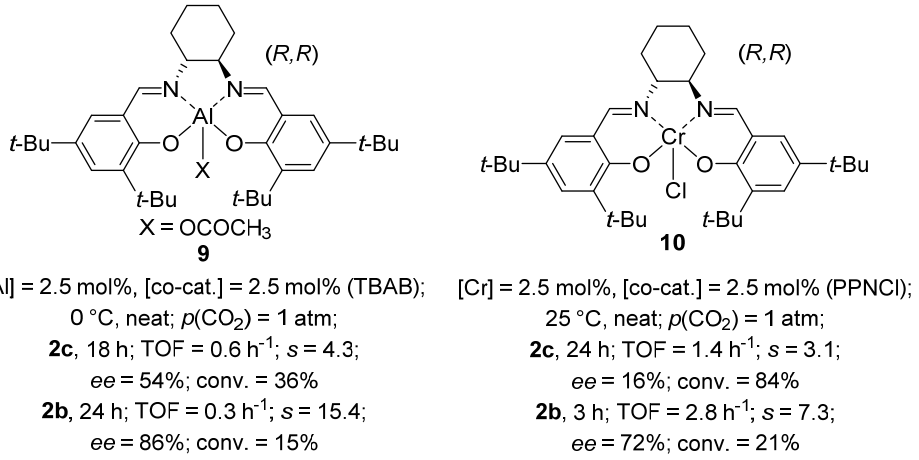

Figure 4. Bifunctional aluminium(III) and chromium(III) salen complexes **9** and **10** for the synthesis of optically active cyclic carbonates.

A novel three-dimensional chiral mixed metal-organic framework (MOF) based on an enantiopure nickel(II)(salen) metalloligand and a tetranuclear cadmium cluster was reported by Jiang and co-workers in 2013 [29]. With each cadmium cluster linked by eight nickel complexes and each nickel complex surrounded by two cadmium clusters, a three-dimensional structure which displayed both high porosity and stability was generated. This material was tested as a catalyst for the enantioselective synthesis of propylene carbonate from racemic propylene oxide using *n*-Bu_4NBr as a co-catalyst at 25 °C and 20 atmospheres of carbon dioxide pressure for 4 h. Under these reaction conditions, propylene carbonate was obtained in 28% conversion and 52% *ee* with a *s* value of 3.8. A recyclability study was performed and showed that no significant loss of activity or selectivity was detected after three cycles. The catalyst was also studied after each cycle via PXRD, with the resulting powder patterns found to be identical to the freshly synthesised MOF. Moreover, analysis of the solution by ICP-AES showed that less than 5% of the nickel and cadmium ions had leached into the reaction mixture. These findings demonstrated that the MOF can act as a very efficient self-supported heterogeneous catalyst for the enantioselective synthesis of propylene carbonate.

2.4. Other Metal Complexes

The first kinetic resolution of epoxides using metal catalysts was reported by Vogt and co-workers in 1993 [30]. The best result was obtained using a combination of (*R*)-(+)-binaphthol in conjunction with zirconium tetrabutoxide as the Lewis acid. 4-(Chloromethyl)-1,3-dioxolan-2-one was obtained from epichlorohydrin in 39% *ee* and with a *s* value of 2.5 at −40 °C and 5 atmospheres of carbon dioxide pressure for 65 h using *n*-Bu_4NI as a co-catalyst. When styrene oxide was used as the substrate, the catalyst system consisting of (*R*)-(+)-binaphthol, titanium isopropoxide and *n*-Bu_4NI as a co-catalyst displayed the highest selectivity. Thus, styrene carbonate was obtained in 35% *ee* and a *s* value of 2.6 at room temperature and 5 atmospheres of carbon dioxide pressure for 24 h.

Optically active niobium(IV) catalysts have been studied by Dibenedetto *et al.* for the enantioselective synthesis of propylene and styrene carbonate from their corresponding racemic epoxides [31]. (*R*)-styrene carbonate was synthesised in up to 74% yield in 22% *ee* using $NbCl_4$(DIOP) [(4*S*,5*S*)-4,5-bis(diphenylphosphino-methyl)-2,2-dimethyl-1,3-dioxolane] as catalyst in dimethylformamide at 135 °C and 50 atmospheres of carbon dioxide pressure for 12 h. The low enantioselectivity is due to the exchange of the enantiopure ligand with the solvent under the reaction conditions.

3. Conclusions

In conclusion, chiral cyclic carbonates are useful synthons in organic synthesis. The most important developments for the enantioselective synthesis of cyclic carbonates via kinetic resolution have been summarized. It is evident that significant advances have been made. However, for the synthesis of chiral cyclic carbonates to be industrially viable, more progress needs to be made.

Acknowledgments: José A. Castro-Osma acknowledges financial support from UCLM-CYTEMA and the Plan Propio de la Universidad de Castilla-La Mancha.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. *Carbon Dioxide as Chemical Feedstock*; Aresta, M., Ed.; Wiley-VCH: Weinheim, Germany, 2010; pp. 1–375.
2. *New and Future Developments in Catalysis, Activation of Carbon Dioxide*; Suib, S.L., Ed.; Elsevier B.V.: Amsterdam, The Netherlands, 2013.
3. *Carbon Dioxide Utilization: Closing the Carbon Cycle*; Styring, P., Ed.; Elsevier B.V.: Amsterdam, The Netherlands, 2014.
4. Peters, M.; Kchler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T.E. Chemical technologies for exploiting and recycling carbon dioxide into the value chain. *ChemSusChem* **2011**, *4*, 1216–1240. [CrossRef] [PubMed]
5. Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the valorization of exhaust carbon: From CO_2 to chemicals, materials, and fuels. Technological use of CO_2. *Chem. Rev.* **2014**, *14*, 1709–1742. [CrossRef] [PubMed]
6. Kasai, N.; Suzuki, T.; Furukawa, Y. Chiral C3 epoxides and halohydrins: Their preparation and synthetic application. *J. Mol. Catal. B Enzym.* **1998**, *4*, 237–252. [CrossRef]
7. Shaikh, A.A.G.; Sivaram, S. Organic carbonates. *Chem. Rev.* **1996**, *96*, 951–976. [CrossRef] [PubMed]
8. Nicolaou, K.C.; Couladouros, E.A.; Nantermet, P.G.; Renaud, J.; Guy, R.K.; Wrasidlo, W. Synthesis of C-2 taxol analogues. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1581–1583. [CrossRef]
9. Chiral Salen Complexes. In *Privileged Chiral Ligands and Catalysts*; Zhou, Q.-L., Ed.; Wiley-VCH: Weinheim, Germany, 2011; pp. 269–273.
10. Paddock, R.L.; Nguyen, S.T. Chiral (salen)Co^{III} catalyst for the synthesis of cyclic carbonates. *Chem. Commun.* **2004**, 1622–1623. [CrossRef] [PubMed]
11. Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. Asymmetric catalysis with CO_2: Direct synthesis of optically active propylene carbonate from racemic epoxides. *J. Am. Chem. Soc.* **2004**, *126*, 3732–3733. [CrossRef] [PubMed]

12. Berkessel, A.; Brandenburg, M. Catalytic asymmetric addition of carbon dioxide to propylene oxide with unprecedented enantoselectivity. *Org. Lett.* **2006**, *8*, 4401–4404. [CrossRef] [PubMed]
13. Chang, T.; Jing, H.-W.; Jin, L.-L.; Qiu, W.-Y. Quaternary onium tribromide catalysed cyclic carbonate synthesis from carbon dioxide and epoxides. *J. Mol. Catal. A* **2007**, *264*, 241–247. [CrossRef]
14. Chen, S.-W.; Kawthekar, R.B.; Kim, G.-J. Efficient catalytic synthesis of optically active cyclic carbonates via coupling reaction of epoxides and carbon dioxide. *Tetrahedron Lett.* **2007**, *48*, 297–300. [CrossRef]
15. Jin, L.-L.; Huang, Y.-Z.; Jing, H.-W.; Chang, T.; Yan, P. Chiral catalysts for the asymmetric cycloaddition of carbon dioxide with epoxides. *Tetrahedron Asymmetry* **2008**, *19*, 1947–1953. [CrossRef]
16. Kawthekar, R.B.; Kim, G.-J. Asymmetric ring opening of epoxides catalysed by novel heterobimetallic Schiff-bases containing transition metal salts. *Bull. Korean Chem. Soc.* **2008**, *29*, 313–318.
17. Zhang, S.-L.; Song, Y.-Y.; Jing, H.-W.; Yan, P.; Cai, Q. Cinchona-derived quaternary ammonium salts-improved asymmetric cycloaddition of CO_2 to epoxides. *Chin. J. Catal.* **2009**, *30*, 1255–1260. [CrossRef]
18. Chang, T.; Jin, L.; Jing, H. Bifunctional chiral catalysts for the synthesis of cyclic carbonates from carbon dixide and epoxides. *ChemCatChem* **2009**, *1*, 379–383. [CrossRef]
19. Zhang, S.; Huang, Y.; Jing, H.; Yao, W.; Yan, P. Chiral ionic liquids improved the asymmetric cycloaddition of CO_2 to epoxides. *Green Chem.* **2009**, *1*, 935–938. [CrossRef]
20. Song, Y.-Y.; Jin, Q.-R.; Zhang, S.-L.; Jing, H.-W.; Zhu, Q.-Q. Chiral metal-containing ionic liquid: Sunthesis and applications in the enantioselective cycloaddition of carbon dioxide to epoxides. *Sci. China Chem.* **2011**, *7*, 1044–1050. [CrossRef]
21. Jang, D.Y.; Jang, H.G.; Kim, G.R.; Kim, G.-J. Synthesis of chiral propylene carbonate via asymmetric ring opening of racemic propylene oxide by carbon dioxide on immobilised cobalt salen catalyst. *Catal. Today* **2012**, *185*, 306–312. [CrossRef]
22. Roy, T.; Kureshy, R.I.; Khan, N.H.; Abdi, S.H.R.; Bajaj, H.C. Asymmetric cycloaddition of CO_2 and an epoxide using recyclable bifunctional polymeric Co(III) salen complexes under mild conditions. *Catal. Sci. Technol.* **2013**, *3*, 2661–2667. [CrossRef]
23. Yan, P.; Jing, H. Catalytic asymmetric cycloaddition of carbon dioxide and propylene oxide using novel chiral polymers of BINOL-salen cobalt(III) salts. *Adv. Synth. Catal.* **2009**, *351*, 1325–1332. [CrossRef]
24. Ren, W.-M.; Wu, G.-P.; Lin, F.; Jiang, J.-Y.; Liu, C.; Luo, Y.; Lu, X.-B. Role of the co-catalyst in the asymmetric coupling of racemic epoxides with CO_2 using multichiral Co(III) complexes: Product selectivity and enantioselectivity. *Chem. Sci.* **2012**, *3*, 2094–2102. [CrossRef]
25. Tanaka, H.; Kitaichi, Y.; Sato, M.; Ikeno, T.; Yamada, T. Enantioselective CO_2 fixation catalysed by optically active cobalt complexes. *Chem. Lett.* **2004**, *6*, 767–677.
26. Yamada, W.; Kitaichi, Y.; Tanaka, H.; Kojima, T.; Sato, M.; Ikeno, T.; Yamada, T. Enantioselective incorporation of carbon dioxide into epoxides catalysed by optically active cobalt complexes. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1391–1401. [CrossRef]
27. North, M.; Quek, S.C.Z.; Pridmore, N.E.; Whitwood, A.C.; Wu, X. Aluminum(salen) complexes as catalysts for the kinetic resolution of terminal epoxides via CO_2 coupling. *ACS Catal.* **2015**, *5*, 3398–3402. [CrossRef]
28. Comerford, J.W.; Ingram, I.D.V.; North, M.; Wu, X. Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings. *Green Chem.* **2015**, *17*, 1966–1987. [CrossRef]
29. Ren, Y.; Cheng, X.; Yang, S.; Qi, C.; Jiang, H.; Mao, Q. A chiral mixed metal-organic framework based on a Ni(saldpen) metalloligand: Synthesis, characterization and catalytic performances. *Dalton Trans.* **2013**, *42*, 9930–9937. [CrossRef] [PubMed]
30. Brunner, M.; Mußmann, L.; Vogt, D. Kinetic resolution of oxiranes by use of chiral Lewis acid catalysts. *Synlett* **1993**, *1993*, 893–894. [CrossRef]
31. Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore, C. Enantioselective synthesis of organic carbonates promoted by Nb(IV) and Nb(V) catalysts. *Appl. Catal. A Gen.* **2003**, *255*, 5–11. [CrossRef]